

Why is the ground state electron configuration for Lithium $1s^22s$?

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Abstract – The electronic ground state for Lithium is $1s^22s$, and not $1s^22p$. The traditional argument for why this is so is based on a screening argument that claims that the $2p$ electron is better shielded by the $1s$ electrons, and therefore higher in energy than the configuration that includes the $2s$ electron. We show that this argument is flawed, and in fact the actual reason for the ordering is because the electron-electron interaction energy is higher for the $2p - 1s$ repulsion than it is for the $2s - 1s$ repulsion.

At the heart of our understanding of atoms, molecules, and solids is an interplay between electron-ion, electron-electron, and ion-ion interactions. Bound states exist *in spite* of repulsive ion-ion interactions so it is really the first two interactions that collaborate to produce conglomerate forms of matter. [1] If we confine our discussion to atoms, then it is clear from the structure of the periodic table that a significant (and appropriate) bias has been applied in favour of the electron-ion interactions. [2] Historically this is no doubt due to two reasons: first, the single electron problem, where electron-electron interactions are absent, has an exact solution (so it is easy to ‘conceptualize’ bound states of many-electron atoms in terms of these solutions), and second, as the atomic number Z of the nucleus increases, the energy associated with the electron-ion interaction (and with the electron kinetic energy) grows as Z^2 , and is therefore dominant. Thus, for the most part, the characteristics of electronic properties of the elements of the periodic table are described in terms of “Hydrogenic states,” i.e. states in which electron-electron interactions are absent.

Nonetheless electron-electron interactions can have an important effect on the properties of elements, particularly when they are introduced into a solid state environment. [3] In this paper we wish to re-examine a particularly simple case, that of the ground state electron configuration in Lithium. The electrons in Lithium are said to reside in the $1s^22s$ (i.e. 2S) state, which is standard short-hand for the antisymmetrized state that is more fully described below. In the absence of electron-electron interactions, the $1s^22s$ and $1s^22p$ (i.e. 2P) states for Lithium are degenerate. An accurate computation, utilizing Hylleraas basis

states, [4] makes it clear that when interactions are fully taken into account, the 2S state indeed has a lower energy, as is clearly observed.

The standard argument for why this is the case proceeds as follows. [5] The higher angular momentum of the $2p$ electron in the 2P state tends to “push” the $2p$ electron further out from the nucleus than is the case with the $2s$ electron in the 2S state. This is based on a semi-classical explanation that invokes the centrifugal force associated with the higher angular momentum of the electron. Two opposing effects now arise. Being further from the centre, the $2p$ electron interacts less with the inner $1s$ electrons; this lowers the energy. However, the $2p$ electron is also screened more from the nucleus, and cannot take full advantage of the electron-ion interaction; this therefore raises the energy. The effects of screening are argued to outweigh the lessened interaction with the inner electrons, and therefore, the 2S is the preferred state.

While both effects are rooted in the electron-electron interaction, the screening argument puts emphasis on the energy lowered through the electron-ion interaction, while the opposing argument clearly emphasizes the direct electron-electron repulsion between the various electrons. [6] In particular, for a small number of particles, and when distances are not large, the distinction between screening and electron-electron interactions is not clear. In this paper, we address this issue and reexamine the traditional argument for Lithium’s preferred state. We will make the claim that it is flawed; contrary to the standard argument espoused in the previous paragraph, screening is somewhat irrelevant and it is the direct electron-electron repulsion between electrons that plays a central role in deciding the

ground state.

The first problem with the standard argument is the claim that “the $2p$ electron is further out from the nucleus than the $2s$ electron.” This is incorrect. It is true that the $2p$ state has a node at the origin, but Kramer’s relation [7] allows one to compute the expectation values

$$\langle r \rangle_{n\ell} = \frac{a}{2} [3n^2 - \ell(\ell+1)], \quad (1)$$

and

$$\langle r^2 \rangle_{n\ell} = \frac{n^2 a^2}{2} [5n^2 - 3\ell(\ell+1) + 1]. \quad (2)$$

From either it follows that the expectation value of the radial extent of the wave function is larger for the $2s$ than for the $2p$ state, contrary to the semi-classical explanation. One can argue that expectation values of the inverse powers of the radial coordinate are more important for the energetics. Then $\langle 1/r \rangle = 1/(n^2 a)$ doesn’t discriminate between the two, while $\langle 1/r^2 \rangle = \frac{1}{n^3 a^2} \frac{1}{\ell+1/2}$ does indeed indicate that the $2p$ state is more extended.

To settle this argument in an unbiased fashion, we follow Ref. [8], and solve for the radial wave function of a particle in an effective potential (Coulomb + centrifugal term), using the one dimensional radial equation. The method of solution presented in the preceding reference requires the use of an infinite square well potential, extending from $r = 0$ to $r = a_{\text{wall}}$, to ‘embed’ the potential of interest. For sufficiently large a_{wall} the low energy eigenvalues and eigenstates are insensitive to the existence of this outer wall. [9] However, in the present work, in order to see which of the two states has larger extension, as measured by the energy, we simply have to lower a_{wall} and monitor which of the two energies, E_{2s} or E_{2p} is affected more. Fig. 1 shows the result of such a calculation, for both the $2s$ and $2p$, and for the $3s$, $3p$, and $3d$ states. There is no question that in either case the energy of the s state is the most affected by the presence of the embedding potential, and hence the most extended. This is in agreement with the expectation based on Eq. (1) or (2). In this sense the $2s$ state in Lithium is more susceptible than the $2p$ state to being screened by the inner $1s$ electrons. Thus, if the naive argument advanced above were correct, the ground state would be primarily $1s^2 2p$, not as observed. We now examine the interactions of the ‘outer’ $n = 2$ electron with the $1s$ electrons.

We first use a simple variational wave function to calculate the energies of the $1s^2 2s$ and $1s^2 2p$ states in Lithium. Our trial wavefunction has the usual determinant form appropriate to the case where we ignore interactions. It is

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{\sqrt{6}} \begin{vmatrix} f(\mathbf{r}_1)\alpha(\mathbf{r}_1) & f(\mathbf{r}_1)\beta(\mathbf{r}_1) & g(\mathbf{r}_1)\alpha(\mathbf{r}_1) \\ f(\mathbf{r}_2)\alpha(\mathbf{r}_2) & f(\mathbf{r}_2)\beta(\mathbf{r}_2) & g(\mathbf{r}_2)\alpha(\mathbf{r}_2) \\ f(\mathbf{r}_3)\alpha(\mathbf{r}_3) & f(\mathbf{r}_3)\beta(\mathbf{r}_3) & g(\mathbf{r}_3)\alpha(\mathbf{r}_3) \end{vmatrix} \quad (3)$$

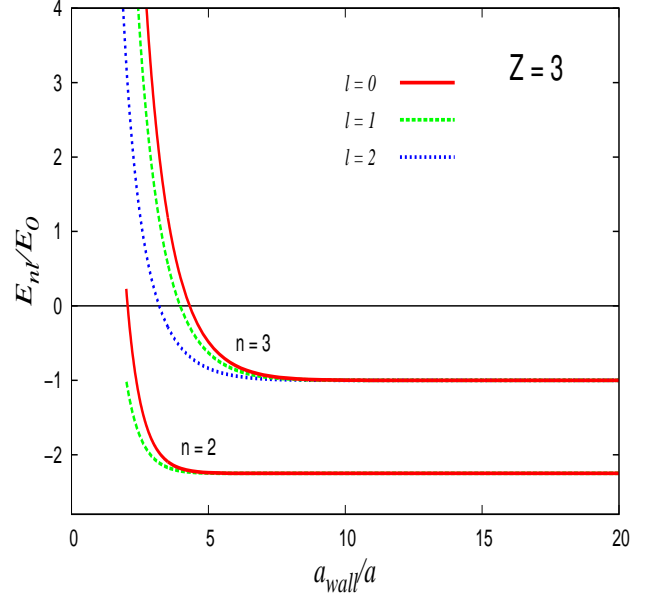


Fig. 1: (Colour online) Energy of the $2s$ vs. the $2p$ states (lower two curves) and $3s$ vs. $3p$ vs. $3d$ states (upper three curves) calculated as a function of the width of an embedding infinite square well potential. For large width, the states are degenerate as expected for the Coulomb potential, but as the width is lowered, the first state affected in either case is the s -state, indicating that it is the more extended of the degenerate set.

where

$$f(\mathbf{r}) = \sqrt{\frac{z_1^3}{\pi a^3}} \exp\left(-\frac{z_1 r}{a}\right) \quad (4)$$

and

$$g(\mathbf{r}) = \begin{cases} \sqrt{\frac{z_2^3}{8\pi a^3}} \left(1 - \frac{z_2 r}{2a}\right) \exp\left(-\frac{z_2 r}{2a}\right), & 1s^2 2s \\ \sqrt{\frac{z_2^3}{32\pi a^3}} \frac{z_2 r}{a} \exp\left(-\frac{z_2 r}{2a}\right) \cos(\theta), & 1s^2 2p \end{cases} \quad (5)$$

Here a is the Bohr radius, and $\alpha(\mathbf{r})$ and $\beta(\mathbf{r})$ represent the usual spin states. For Lithium, $z_1 = z_2 = 3$; here they are retained as variational parameters. We use this trial wavefunction to place an upper limit on the energy of each state. The nonrelativistic Hamiltonian for the Lithium atom is

$$\begin{aligned} H &= H_{\text{kinetic}} + H_{\text{nuclear}} + H_{\text{interaction}} \\ &= \frac{-\hbar^2}{2m} (\nabla_1^2 + \nabla_2^2 + \nabla_3^2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{Z}{r_1} + \frac{Z}{r_2} + \frac{Z}{r_3} \right) \\ &\quad + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_3|} + \frac{1}{|\mathbf{r}_2 - \mathbf{r}_3|} \right) \end{aligned} \quad (6)$$

where the terms corresponding to each part of the Hamiltonian should be clear. Note that Z is the nuclear charge. Contributions to the energy are divided into the following categories: $K \equiv \langle H_{\text{kinetic}} \rangle$, $U_{\text{nuclear}} \equiv \langle H_{\text{nuclear}} \rangle$,

and U_{1s1s} , U_{1s2s} , U_{1s2p} , Ex_{1s2s} , and Ex_{1s2p} refer to the direct Coulomb and exchange energies for the orbitals listed. Then the total energies for each state are

$$E_S = K + U_{\text{nuclear}} + U_{1s1s} + 2U_{1s2s} + Ex_{1s2s} \quad (7)$$

$$E_P = K + U_{\text{nuclear}} + U_{1s1s} + 2U_{1s2p} + Ex_{1s2p}. \quad (8)$$

Calculations are straightforward; with $E_0 \equiv \hbar^2/(2ma^2)$ ($= 1$ Rydberg), the three terms in common for the two states are

$$\frac{K}{E_0} = 2z_1^2 + \frac{1}{4}z_2^2, \quad (9)$$

$$\frac{U_{\text{nuclear}}}{E_0} = -Z \left(4z_1 + \frac{1}{2}z_2 \right) \quad (10)$$

and

$$\frac{U_{1s1s}}{E_0} = \frac{5}{4}z_1. \quad (11)$$

Then for the two trial states, we have

$$\begin{aligned} \frac{U_{1s2s}}{E_0} &= 2 \int |f(\mathbf{r}_1)|^2 \frac{a}{|\mathbf{r}_1 - \mathbf{r}_2|} |g(\mathbf{r}_2)|^2 d^3r_1 d^3r_2 \\ &= 2z_1 z_2 \frac{(8z_1^4 + 20z_1^3 z_2 + 12z_1^2 z_2^2 + 10z_1 z_2^3 + z_2^4)}{(2z_1 + z_2)^5} \end{aligned} \quad (12)$$

and

$$\begin{aligned} \frac{U_{1s2p}}{E_0} &= 2 \int |f(\mathbf{r}_1)|^2 \frac{a}{|\mathbf{r}_1 - \mathbf{r}_2|} |g(\mathbf{r}_2)|^2 d^3r_1 d^3r_2 \\ &= \frac{U_{1s2s}}{E_0} + \frac{16z_1^3 z_2^3}{(2z_1 + z_2)^5}, \end{aligned} \quad (13)$$

respectively. The exchange terms (Ex_{1s2s} and Ex_{1s2p}) arise from consideration of the full antisymmetric wavefunction. For the two trial states, the exchange terms are

$$\begin{aligned} \frac{Ex_{1s2s}}{E_0} &= -8192z_1^4 z_2^3 \left\{ \frac{(z_1 - 2Z)(z_1 - z_2)^2}{4(2z_1 + z_2)^8} \right. \\ &+ \frac{(z_1 - z_2)(z_1 z_2(4z_1 - z_2) - Z(4z_1^2 - z_2^2))}{8z_1(2z_1 + z_2)^8} \\ &+ \frac{(z_1 - z_2)(264z_1^4 - 28z_1^3 z_2 - 86z_1^2 z_2^2 - 21z_1 z_2^3 - z_2^4)}{(2z_1 + z_2)^7(6z_1 + z_2)^4} \\ &\left. + \frac{(20z_1^2 - 30z_1 z_2 + 13z_2^2)}{256z_1(2z_1 + z_2)^7} \right\}, \end{aligned} \quad (14)$$

and

$$\frac{Ex_{1s2p}}{E_0} = -\frac{224}{3} \frac{z_1^3 z_2^5}{(2z_1 + z_2)^7}, \quad (15)$$

respectively. In addition, the first state is not normalized. Therefore

$$\langle \Psi_S | \Psi_S \rangle = 1 - 2048z_1^3 z_2^3 \frac{(z_1 - z_2)^2}{(2z_1 + z_2)^8} \quad (16)$$

Term	Perturbative (eV)		Variational (eV)	
	$1s^2 2s$	$1s^2 2p$	$1s^2 2s$	$1s^2 2p$
K	275.5	275.5	212.1	200.0
U_{nuclear}	-551.0	-551.0	-486.7	-459.9
U_{1s1s}	51.0	51.0	46.6	45.7
U_{1s2s}	17.1	-	11.4	-
U_{1s2p}	-	19.8	-	7.1
$Exch_{1s2s}$	-1.8	-	3.9	-
$Exch_{1s2p}$	-	-1.4	-	-0.1
$\langle \Psi \Psi \rangle$	1	1	0.98	1
Total	-192.0	-186.3	-201.2	-200.0

Table 1: Energies found for each term using a perturbative calculation ($z_1 = z_2 = 3$) and a variational calculation using Eqs. (7) and (8). In both cases $Z = 3$. The optimal z_1 and z_2 values from the variational calculation are given in the text. The actual values for the $1s^2 2s$ and $1s^2 2p$ energies are -203.5 eV and -201.6 eV respectively. [4]

The trial wave function remains normalized for the 2P state, i.e. $\langle \Psi_P | \Psi_P \rangle = 1$.

If the variational parameters are fixed at $z_1 = z_2 = 3$, the calculation may be considered as a perturbative calculation, where the electron-electron interactions act as the perturbation; these energies are listed in Table 1.

More accurate energy estimates may be found if z_1 and z_2 are taken as variational parameters. Minimization of Eq. (7) yields $z_1 \approx 2.68$ and $z_2 \approx 1.87$, while for the 2P state given by Eq. (8) we find $z_1 \approx 2.69$ and $z_2 \approx 1.05$. The proximity of the last number to $Z - 2 = 1$, and the relative accuracy of the variational calculation (differences of 1.1% and 0.8% for the two states) no doubt combine to inspire the traditional screening argument.

However, these variational calculations implicitly account for electron configurations beyond the $n = 1$ and $n = 2$ states under consideration here. More straightforwardly, inspection of the perturbation-like calculations in Table 1 indicates that the electron-electron interaction energy between the $1s$ and $2p$ states ($2(U_{1s2p} + Ex_{1s2p}) \approx 36.8$ eV) is considerably higher than that between the $1s$ and $2s$ states ($2(U_{1s2s} + Ex_{1s2s}) \approx 30.6$ eV). When one goes beyond perturbation theory, both wave functions expand by incorporating higher energy configurations; these serve the purpose of allowing the electrons to avoid one another more efficiently, and in so doing, the $1s$ electrons effectively ‘screen’ the $2s$ or $2p$ electron. So in an attempt to ameliorate the (rather large) electron-electron energy cost for the $2p$ electron, the variational calculation simply places it further from the nucleus, and succeeds in lowering this energy, but at a cost of what we have called U_{nuclear} (-551.0 gets raised to -459.9). The same thing happens for the $2s$ electron, but to a lesser extent, in part

because the $2s$ electron is already further extended than the $2p$ electron. Nonetheless, this does not succeed in reversing what was evident from the first two columns — the $1s^2 2p$ state simply has a higher electron-electron energy compared to the $1s^2 2s$ state, and therefore the latter has lower energy.

Phrased this way, it should be evident that ‘screening’ is the ‘sacrifice’ one makes to lower the overall energy. In both the $2s$ and the $2p$ case, lowering the overall energy was accompanied by screening, i.e. a raising of U_{nuclear} (while the overall energy decreased). This is qualitatively different than the standard argument that says that the $2p$ state is more screened to begin with (false!) and therefore its energy is higher.

In summary, we have argued that the ground state electron configuration for Lithium is $1s^2 2s$, and not $1s^2 2p$ in spite of screening, not *because of* screening. Expansion of an electron cloud surrounding a nucleus generally occurs in an effort to minimize the Coulomb repulsion experienced by these electrons. [10] It follows that the more repulsive these interactions are, the more will the electrons expand away from one another. In so doing, they also become more efficiently screened by the remaining electrons; this is a sacrifice that is made in spite of the electron-ion energy increase, because the total is thereby decreased. The original and incorrect argument stated that the Hydrogenic $2p$ state is more screened than the Hydrogenic $2s$ state, and this is why the latter results in a lower energy. Our argument clearly attributes the deciding factor to the electron-electron repulsion, and increased screening is a necessary (energy raising) by-product that is nonetheless tolerated by the ground state.

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REFERENCES

- [1] We single out the ion(s) in this discussion because they are much more massive than the electrons; in other words we assume a Born-Oppenheimer approximation.
- [2] Note that in the case of solids the dilemma of focussing on electron-ion vs. electron-electron interactions faced Bloch in his initial formulation of “Bloch’s Theorem;” he focussed on the former basically because it was “the simplest assumption.” See F. Bloch, Proc. R. Soc. Lond. **A371**, 24 (1980), and, for a more recent discussion, J.E. Hirsch, Int. J. Mod. Phys. **B23**, 3035 (2009).
- [3] This statement is meant to have more content than might appear at first glance; it goes without saying that electron-electron interactions result in subtle correlations in solids from which new phases of matter, such as magnetism or superconductivity may result. What we mean here, however, is that the atomic (i.e. local) properties of electronic

states can be significantly altered by electron-electron interactions. An example is the necessity of accounting for expanded atomic orbitals, when those orbitals are doubly occupied, as first suggested clearly by J.E. Hirsch, Phys. Rev. Lett. **87**, 206402 (2001).

- [4] See, for example, Z.-C. Yan and G.W.F. Drake, Phys. Rev. A **52**, 3711 (1995), and more recently L.M. Wang, Z.-C. Yan, H.X. Qiao, and G.W.F. Drake, Phys. Rev. A **85**, 052513 (2012), and references therein.
- [5] This argument is given in many standard texts, for example, D. J. Griffiths, *Introduction to Quantum Mechanics* (Pearson/Prentice Hall, Upper Saddle River, NJ, 2005), 2nd edition (see page 215).
- [6] Note that in the case of Helium, while the second electron is primarily in the $1s$ state because that minimizes the electron-ion energy, there is nonetheless almost 10% probability that either electron is *not* in the $1s$ level, specifically because this lowers electron-electron interaction energy. Thus in the case of Helium, screening (i.e. some of the electron cloud is pushed further out) occurs to lower the energy, not the other way around.
- [7] See Ref. [5], p. 289, problems 6.34 and 6.35, where these relations are derived.
- [8] B.A. Jugdutt and F. Marsiglio, “Solving for 3D potentials using matrix mechanics with a truncated basis set,” unpublished.
- [9] The existence of the wall at $r = 0$ does not effect the solution since the radial wave function $u(r) \equiv rR(r)$ is required to be zero there anyways.
- [10] See the reference in Ref. [3], along with J.E. Hirsch, Phys. Rev. **B65**, 184502 (2002).